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HIGH PRODUCTION VOLUME (HPV) CHEMICAL CHALLENGE PROGRAM

**TEST PLAN FOR RECLAIMED SUBSTANCES: STREAMS
CONTAINING NAPHTHENIC ACIDS, PHENOLICS, DISULFIDES,
ACIDS OR CAUSTICS**

Submitted to the US EPA

by

**The American Petroleum Institute
Petroleum HPV Testing Group**

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RECLAIMED SUBSTANCES TEST PLAN

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PLAIN LANGUAGE SUMMARY

The high production volume (HPV) chemical substances addressed in this test plan are all intermediate streams or by-products that result from the refining of petroleum products. Most of these substances are not sold as products. Many are “spent” solutions that are sent to a chemical processor for recycling. For purposes of evaluating the sponsored substances, the Testing Group has created four categories: streams containing naphthenic acids, streams containing phenolics, streams containing disulfides, and streams containing acids or caustics. It is the Testing Group’s opinion that only one category, naphthenic acids, should be evaluated for the adequacy of health and environmental effects data.

Naphthenic acids are extracted from kerosene and diesel streams in the refinery to improve the burning qualities and storage properties of the finished products. The major uses of naphthenic acids are as oil-soluble metal soaps for driers and other catalysts, wood preservatives, tire cord adhesion promoters, and in amine derivatives for corrosion inhibitors. The available data show that naphthenic acids have a low to moderate degree of acute mammalian toxicity, and do not produce genetic toxicity in laboratory cell culture studies.

The Testing Group has determined that additional studies are necessary to adequately characterize the hazard of naphthenic acids. They are proposing that a combined repeated-dose, reproductive/developmental toxicity screening test be conducted and that genetic toxicity be evaluated in that study. In addition, toxicity testing in fish, aquatic invertebrates, and algae will be conducted to address the potential aquatic toxicity of these materials. There is adequate data on the physicochemical and environmental fate of naphthenic acids.

DESCRIPTION OF RECLAIMED SUBSTANCES CATEGORIES

All of the sponsored HPV substances addressed by this test plan are intermediate streams or by-products from the refining of petroleum products. In addition, most of the substances are in some way associated with the use of caustic sodium hydroxide solutions to remove sulfur impurities from various process streams. Removal of sulfur impurities is important in petroleum refining to improve the burning qualities, storage stability, and odor of finished fuel products.

Caustic treatment also removes other constituents (some unintentionally) from the fuels including naphthenic acids and phenolics. Because of the low concentration of these impurities, it is not economical for refiners to recover and sell these chemical substances. However, spent caustics are routinely sent to a specialized chemical processor where some of them can be recovered and sold as products.

For purposes of evaluating the sponsored substances, the Testing Group has created four categories: streams containing naphthenic acids, streams containing phenolics, streams

containing disulfides, and streams containing acids or caustics. They are discussed individually below:

Streams Containing Naphthenic Acids

Naphthenic acids are a naturally occurring, complex mixture of cycloaliphatic carboxylic acids recovered from petroleum distillates. The naphthenic acid containing chemical substances sponsored by the Testing Group are as follows:

61790-13-4

Naphthenic acids, sodium salts

064754-89-8

Naphthenic acids (petroleum), crude

A complex combination of compounds, predominantly naturally occurring organic acids, obtained from petroleum fractions by saponification and acidification. It consists predominantly of compounds which contain carboxylic acid functional groups and five- to six-member naphthenic rings in their molecular structures. Phenolic compounds and acidic sulfur compounds may also be present.

1338-24-5

Naphthenic acids

Naphthenic acids, as used in the petroleum industry, refers collectively to all of the carboxylic acids present in crude oil. Naphthenic acids (CASRN 1338-24-5) are classified as monobasic carboxylic acids of the general formula RCOOH , where R represents the naphthene moiety consisting of cyclopentane and cyclohexane derivatives. Naphthenic acids are composed predominantly of alkyl-substituted cycloaliphatic carboxylic acids, with smaller amounts of acyclic aliphatic acids. The cycloaliphatic acids include single and fused multiple cyclopentane and cyclohexane rings. The carboxyl group is usually attached to a side chain rather than directly to the ring. Aromatic, olefinic, hydroxy and dibasic acids are present as minor components (Brient et al, 1995).

Although the presence of naphthenic acids has been established in almost all types of crude oil, only certain naphthenic and asphalt based crudes contain amounts that are high enough to require treatment in order to meet specifications. Naphthenic acids recovered from refinery streams occur naturally in the crude oil and are not formed during the refining process. Heavy crudes have the highest acid content, and paraffinic crudes usually have low acid content.

Naphthenic acids are obtained by caustic extraction of petroleum distillates, primarily kerosene and diesel fractions. In addition to reducing corrosion in the refinery, the caustic wash of the distillates is necessary to improve the burning qualities, storage stability, and odor of the finished kerosene and diesel fuels. The commercial production of naphthenic acid from petroleum is based on the formation of sodium naphthenates when the petroleum distillates are treated with sodium hydroxide caustic. Since this reaction occurs *in situ*, naphthenic acids, sodium salts (CASRN 61790-13-4) is considered an intermediate stream in the production of naphthenic acid. The sodium

naphthenate-containing solutions contain approximately 5-15% sodium naphthenate, 0-0.5% sodium mercaptide and 3-4% sodium hydroxide in water, and the pH exceeds 12-13. These caustic solutions are typically sent to a specialized facility where they undergo further processing to recover the naphthenic acids.

The first step in recovery of the naphthenic acid involves “springing” (acidulating) the caustic solutions produced in the refinery to recover the organic acids. The resulting intermediate stream is crude naphthenic acids (petroleum), CASRN 64754-89-8. This is followed by a series of additional refining steps, including distillation, to recover the naphthenic acids.

The major uses of naphthenic acids are as oil-soluble metal soaps for driers and other catalysts, wood preservatives, tire cord adhesion promoters, and in amine derivatives for corrosion inhibitors. The petroleum industry uses naphthenic acid amine derivatives as surfactants for enhanced oil recovery and as corrosion inhibitors for refineries, pipelines, and downhole use.

Summary – of the three substances sponsored in this sub-category, naphthenic acids (CASRN 1338-24-5) is the only material sold commercially. The other two are intermediates in the production of naphthenic acids. Since all contain the same basic naphthenic acid species, information on the health and environmental effects of naphthenic acids can be extrapolated to the two intermediate streams. The Testing Group has reviewed the available health, environmental and physicochemical information on naphthenic acids and has used this material to represent the category.

Streams Containing Phenolics

Cresols, xylenols and cresylic acids are produced during the catalytic cracking process and are concentrated in the middle distillate streams (approximately 350-700 degrees F) in the refinery. When any of these middle distillate streams are treated for mercaptan removal by caustic treating, cresols, xylenols and cresylic acids are co-extracted and become part of the caustic solutions. These caustic solutions are used as feedstocks to produce a number of finished products that are intermediates in the manufacture of a wide variety of industrial products such as resins, flame retardants, antioxidants, varnishes and disinfectants.

“Cresols” refer to any of the three isomers of methylphenol (C_7H_8O) or combinations thereof. “Xylenols” are any of the six isomers of dimethylphenol ($C_8H_{10}O$) and their various combinations. “Cresylic acid” is a generic term referring to combinations of both cresols and xylenols along with phenol or various other alkylphenols (ethylphenols, propylphenols, etc.).

The cresylate-containing chemical substances sponsored by the Testing Group are as follows:

68988-99-8

Phenols, sodium salts, mixed with sulphur comp; gasoline alky scrubber residues

“A complex combination of phenolic compounds and sulfur compounds obtained from the treatment of gasoline with aqueous alkali at the catalytic cracking unit. It consists primarily of sodium salts of phenols, water neutral oils and sulfur compounds.”

This material is the spent caustic solution formed when catalytic cracked distillates are caustic treated to remove mercaptan sulfur compounds (the phenolic species, now in the form of sodium salts, i.e. cresylates, come along for the ride). Historically, this material has been the major feedstock at the facility where cresylic acid products are produced. This stream typically contains 10-15% sodium cresylates, 1% sodium mercaptide, 7.5% sodium hydroxide and 77-82% water, with a pH of 13.

64743-03-9

Phenols, (petroleum)

Crude phenolic compounds (petroleum) “A complex combination of organic compounds, predominantly phenol, cresols, xlenols and other alkylated phenols obtained primarily from cracked naphtha or distillate streams by alkaline extraction”

This material describes the intermediate product obtained when phenolic containing caustic solutions are acidified, thus “springing” cresylate compounds – converting them from a sodium salt to the organic form which then separates from the alkaline material. Further processing of this “sprung” organic mixture is necessary to separate the individual chemical compounds from the mixture. This process is not commonly carried out in refineries; rather the caustic solutions are sent to a specialized facility for conversion of the cresylates and recovery of the phenolic products. This intermediate stream typically contains about 20% phenol, 40% cresols (o-, m-, and p-isomers), 30% xlenols (6 isomers) and 10% alkylated phenols.

Summary - It is the HPV Testing Group’s conclusion that none of the materials in this subcategory should be evaluated in the HPV program. The first stream (68988-99-8) is a spent caustic and should not be used in animal studies for obvious reasons. Because it is a byproduct, and processed only by a few companies, its potential for human and environmental exposure is very limited.

The second stream (64743-03-9) is also one in which there is limited potential for human or environmental exposure since it is a non-isolated intermediate in the process used to recover cresylic acid components. As a non-isolated intermediate, its reporting on the Inventory Update Report was probably in error. That being the case, the stream would not be considered a “manufactured” chemical substance and not eligible for inclusion in the HPV program. In addition, EPA’s Tier 2 gasoline requirements will result in most refiners replacing caustic extraction with more efficient sulfur removal technologies.

It should also be noted that phenols and cresols have been the subject of American Chemistry Council Chemstar panels. While the testing group did not evaluate these chemicals for data adequacy, it is believed that there is substantial information on their potential health and environmental hazards.

Streams Containing Disulfides

Petroleum crude oils contain organic sulfur compounds (mercaptans), dissolved hydrogen sulfide and sometimes suspended sulfur. High concentrations of sulfur compounds are undesirable in petroleum refining since they can be corrosive, reduce the service life of certain catalysts, and degrade the quality of finished products by changing their color or by giving them an unpleasant odor. High sulfur also increases the formation of sulfates and sulfites during the combustion of petroleum fuels. Mercaptans have the general formula $R - S - H$, where R represents an aliphatic or cyclic radical.

Removing mercaptans from various streams is referred to as sweetening and is used most commonly for gas, naphtha and kerosene range streams. Sweetening can be effected in one of two modes, extractive and non-extractive. In the extractive mode, mercaptans are caustic extracted from the hydrocarbon stream and later oxidized to disulfides. In the non-extractive mode the caustic treatment is carried out in the additional presence of oxygen (air) and the mercaptides are oxidized *in situ* to disulfides which are reverse extracted back into the hydrocarbon stream. In the extractive version, sodium hydroxide (caustic) treatment of the gas or naphtha streams will remove the mercaptan sulfur compounds as mercaptides in the caustic solution and in a separate process step the mercaptides in the caustic solution are oxidized to disulfides.

Disulfides have the general formula $R - S - S - R$, and are not corrosive. The disulfides are typically removed from the caustic by solvent extraction. They are not typically separated by refiners for commercial sale because the small volumes produced are not economical for commercial production. The solvent solutions containing the disulfides are typically recycled in the refinery upstream of a hydrotreater which results in destruction of the disulfide substances. They may also be burned as a refinery fuel. In addition, there are only limited uses for these materials. The primary outlet for disulfides is the manufacture of sulfuric acid where they are burned for sulfur recovery. They have also been used as rubber reclaim solvents and as downhole desulfurization solvents in the oil patch.

As described above, EPA's requirements for reducing the sulfur level in fuels has resulted in an increase in the use of hydrotreating and other sulfur removal technologies, since caustic treatment is not as efficient. This has decreased the amount of spent caustic being generated. Merichem is currently the only company that still handles phenolic containing caustics as feedstocks in its plant to make cresylic acid products. As a result of the decrease in feedstock availability, they will be changing their process in 2005 and no longer manufacturing disulfide oils.

The disulfide-containing chemical substances sponsored by the Testing Group are as follows:

68334-01-0

Disulfides, alkylaryl dialkyl, petroleum refinery spent caustic oxidation products

“A complex combination of disulfides obtained from oxidation of spent caustic from the caustic treatment of straight run naphtha and catalytic cracked naphtha.”

This material, if produced by a refiner, represents the product obtained by oxidizing the spent caustic used in removing mercaptans from straight run and catalytic cracked naphtha streams. It is typically recycled on site or burned as a fuel. It is a hydrocarbon material and not corrosive. As mentioned above, disulfide oils are often produced in admixture with a solvent and if recycled in the refinery, is typically inserted upstream of a hydrotreater or other process that removes the sulfur. It is not sold as a product.

68955-96-4

Disulfides, dialkyl and di-Ph, naphtha sweetening

"A complex combination of disulfides obtained by subjecting naphtha or gases from various refinery processes to a sweetening process to convert mercaptans. The dialkyl disulfides have carbon numbers predominantly in the range of C1 through C4.”

This material represents the mixture of disulfides that results from caustic extraction of naphtha streams, followed by oxidation of the resulting caustic solution containing the extracted mercaptides. In refineries, the disulfides are either recycled back into the refinery or burned as fuel. It is not sold as a product.

68513-62-2

Disulfides, C5-12-alkyl

This material represents the disulfides resulting from sweetening of heavy straight run or cracked naphtha streams. Only one refiner in the HPV testing group reported this material. They indicated that the material is completely recycled back into the refinery and not sold as a commercial product.

68920-64-9

Disulfides, di-C1-2-alkyl

This CASRN refers to the disulfides obtained from sweetening a light hydrocarbon gas or LPG type streams. The mercaptans in the stream are removed by caustic extraction and thereafter the caustic solution is oxidized with air to form the disulfides, which may be facilitated in their separation by the use of a solvent. The resulting disulfide/solvent mixture is either recycled within the refinery or burned as a fuel. This occurs in a closed system. This material is not sold by refiners as a commercial product.

Summary – All four materials described in this subcategory are mixtures of disulfides (organic materials) represented by the formula R-S-S-R. All four, if produced in the refinery, are either recycled within the refinery or burned as a fuel. None of these materials are sold as a product of the refinery. The disulfides produced by Merichem, the only company that reclaims them from spent caustics, are subsequently destroyed in the manufacture of sulfuric acid. Their manufacture of disulfides will cease in 2005.

It is the HPV Testing Group's conclusion that none of the materials in this subcategory should be evaluated in the HPV program.

Streams Containing Acids or Caustics

This subcategory contains materials that are either highly acidic or highly alkaline. These materials are all byproducts of petroleum processing and are not sold as consumer products.

68815-21-4

Tar acids, cresylic, sodium salts, caustic solutions.

This material is a spent caustic solution obtained from the neutralization of acidic petroleum distillate streams. Its composition is predominantly sodium salts of cresylic and phenolic acids, sodium hydroxide and water. This material is either sent to a chemical processor for recovery of organic acids or disposed of as a waste. It is highly alkaline and corrosive.

064742-24-1

Sludges (petroleum), acid

A complex combination of sulfuric and sulfonic acids, water, esters and high molecular weight organic compounds such as polymers of olefinic hydrocarbons. It is formed during the treating of petroleum fractions with sulfuric acid.

This material was only reported by one refiner. Sulfuric acid is used as a catalyst in the alkylation process. While much of the acid is recycled back through the acid plant for reuse, a stream of contaminated acid is removed to reduce the buildup of impurities. The spent acid stream is used only for pH control at the refinery's wastewater plant and none is shipped off-site. The sulfuric acid concentration of this material is between 90-93%.

064742-40-1

Neutralizing agents (petroleum), spent sodium hydroxide

A complex combination consisting predominantly of water and containing sodium hydroxide and organic and inorganic sodium salts.

This material, as described above, is produced by treating certain hydrocarbon streams for mercaptan removal. Some of the caustics come from the caustic treating units while others come from regeneration units where the caustics are initially oxidized to remove the extracted sulfur compounds as disulfides. These units return most of the caustic to the treating unit, but there is a draw down required to keep the sulfides from concentrating to the point where the regenerated caustic is no longer useful. The typical concentration of the spent caustic is approximately 4 % sodium sulfide, 5 % sodium hydroxide, 1% sodium mercaptides, and 90% water.

Summary – All of these materials are highly alkaline or acidic by-products of various petroleum refining processes. It is the Testing Group's conclusion that none of the materials in this subcategory should be evaluated in the HPV program.

CATEGORY RATIONALE

Because the majority of the substances in these categories were intermediate streams or spent acids and caustics, it was the decision of the Testing Group that only one of the four categories, streams containing naphthenic acids, be evaluated for health and environmental effects. Of the three substances sponsored in this subcategory, naphthenic acids (CASRN 1338-24-5) is the only material sold commercially. The other two are intermediates in the production of naphthenic acids. Since all contain the same basic naphthenic acid species, information on the health and environmental effects of naphthenic acids can be extrapolated to the two intermediate streams. The Testing Group has reviewed the available health, environmental and physicochemical information on naphthenic acids and has used this material to represent the category.

EVALUATION OF EXISTING HEALTH EFFECTS DATA AND PROPOSED TESTING

For the reasons stated above, the only reclaimed substances subcategory being evaluated for existing health effects data is naphthenic acids. This section addresses the mammalian toxicity endpoints by:

1. Searching the literature for existing data and evaluating existing studies for adequacy;
2. Using read-across information whenever possible of similar materials; and
3. Proposing toxicity testing needed, when necessary to fill data gaps.

The endpoints include: acute toxicity, repeated dose toxicity, *in vitro* and *in vivo* mutagenicity, and reproductive/developmental toxicity. Where complete studies were not available for review (e.g., technical meeting abstracts or poster presentations), these data are summarized here and the source citations are provided in the Reference section of this document. In addition, information from relevant non-OECD SIDS/HPV Chemical Program protocols is cited and judged for its applicability to the Test Plan.

Streams Containing Naphthenic Acids

Acute Toxicity

The acute toxicity of naphthenic acids has been investigated in experimental animals via the oral and dermal routes of exposure. In male rats, the acute oral LD₅₀ of a naphthenic acids sample was determined to be 5.88 g/kg body weight (Exxon, 1979b). Although no deaths were observed in the low dose animals (1.0 and 2.15 g/kg), a number of symptoms of toxicity were noted. In a previous acute oral screening LD₅₀ study, both female and male rats were administered 10 g/kg, after which all the animals died (Exxon, 1979b). In rabbits, the same material had a dermal LD₅₀ of >3.16 g/kg (Exxon, 1979c). Toxic signs were observed and the skin reactions were judged to be moderately to severely irritating (Exxon, 1980b). This material was also determined to be moderately irritating to the eyes of rabbits (Exxon, 1979d; Exxon, 1980b). An inhalation study in rats, mice and guinea pigs at doses of 0.63 mg/l (near saturation level) for 6 hours was reported to

produce no deaths or signs of systemic toxicity (Exxon, 1987); however, experimental details of this study could not be verified.

Oral LD₅₀s of 3.0 g/kg and 5.2 g/kg were observed in rats dosed with a naphthenic acids fraction from crude kerosene acids or mixed crude acids respectively (Rockhold, 1955). In another study, the oral LD₅₀ of naphthenic acids was determined to be 3550 mg/kg in young white male mice (Pennisi and Lynch, 1977 -abstract only). The quality of this study cannot be verified since the report does not provide complete experimental details.

In a study using a non-OECD SIDS/HPV Chemical Program protocol, adult female rats received a single oral dose of naphthenic acids of 3, 30, or 300 mg/kg body weight while adult male rats received 300 mg/kg. After 14 days, treatment-related effects on the cardiovascular system and liver, in particular, were observed in the high dose groups of both sexes (Rogers et al, 2002a). In addition, significant cerebral hemorrhages were observed in male rats.

Summary: No additional testing is planned. Available data suggest a low order of acute toxicity, with significant systemic toxicity at doses that are not lethal. The Testing Group has determined that the data are of sufficient quality to estimate the acute toxicity potential of naphthenic acids.

Repeat-Dose Toxicity

A 90-day oral gavage study (non-OECD SIDS/HPV Chemical Program protocol) in female rats of naphthenic acids at doses of 0.6, 6, and 60 mg/kg/day resulted in a number of apparent treatment-related effects (Rogers, et al, 2002a). These include the following: body weight decreases, increases in relative liver, brain and kidney weights, plasma biochemical differences indicating the liver as a target organ, and increased glycogen storage in the liver. All effects occurred in the high dose groups. In addition, there was a severe seizure activity observed in high and mid-dose animals after day 40. The authors noted that there were milder episodes observed in the low-dose and control groups as well. The limited number of organs examined and the absence of male data limit the usefulness of this study in estimating repeat-dose toxicity.

Male mice administered an oral dose of naphthenic acid at 1000 mg/kg/day for 30 days demonstrated signs of CNS depression, hematological changes, weight loss (leading eventually to death due to respiratory arrest), gross morphological changes in the liver and stomach, and histomorphological changes in a few unidentified, selected organs (Pennisi and Lynch, 1977 -abstract only). The quality of this study cannot be verified since the report does not provide complete experimental details.

In a two-year dermal carcinogenicity study in female mice (no male data), calcium naphthenate (the calcium salt of naphthenic acids) in mineral oil (unspecified concentration) resulted in a carcinogenic response after 392 days of treatment. No metastatic tumors were present. (U.S.EPA, 2003 - Shell, 1982). Only brief reports of this study are available, consequently the quality of the study cannot be evaluated.

Summary: The Testing Group thinks the existing repeat-dose toxicity studies on naphthenic acids are not of sufficient quality to adequately address this endpoint. Consequently, naphthenic acid will be tested (route to be determined) using a 28-day combined, repeated-dose and reproductive/developmental toxicity screening protocol (OECD Test Guideline 422). It is the intention of the Testing Group to augment the 28-day dermal study with the *in vivo* micronuclei assay to provide additional information on the genotoxicity of naphthenic acid (See “In Vivo Mutagenicity”).

In Vitro Mutagenicity

Although no studies were available on the *in vitro* genotoxicity of naphthenic acid, there are data on the calcium and sodium salts. NTP studies indicate that neither calcium naphthenate nor sodium naphthenate were mutagenic in *S. typhimurium* with or without S9 (NTP, 2003). Sodium naphthenate did not produce effects in hamster ovary cells, but was positive in a sister chromatid exchange assay. Calcium naphthenate was not mutagenic in *Escherichia coli* or yeast (*Saccharomyces cerevisiae*), and did not cause chromosome damage in rat liver cells (BIBRA, 1999). The details of these calcium naphthenate studies could not be verified.

Summary: No additional testing is planned. Available NTP data on the sodium and calcium salts of naphthenic acid suggest a low potential for genotoxicity. The Testing Group has determined that the data are of sufficient quality to estimate the *in vitro* genotoxic potential of naphthenic acids.

In Vivo Mutagenicity

No studies have been reported on the *in vivo* genotoxicity of naphthenic acids or related materials.

While the Testing Group shares the desire to limit animal testing by using *in vitro* methodologies when possible, it decided to conduct the *in vivo* micronucleus test because it could be performed using animals that were already included in the repeat dose 28-day study, and it eliminates the need to perform an additional study solely for the purpose of studying *in vivo* genotoxicity.

Summary: Naphthenic acid will be tested in the *in vivo* mammalian erythrocyte micronucleus test (OECD 474). The *in vivo* micronucleus test will be included in the 28-day repeat dose study on naphthenic acid (see “Repeat-Dose Toxicity” section).

Reproductive/Developmental Toxicity

No studies have been reported on the reproductive toxicity of naphthenic acids. In a non-OECD SIDS/HPV Chemical Program protocol, neat calcium naphthenate solution (concentration not provided) was applied to male rabbits (10 total), which were subsequently mated to untreated females (2 total). No significant effects were seen in reproductive parameters or abnormalities in the male reproductive tract. The description and results of this study are in abstract form only (U.S. EPA, 2003 – website).

Naphthenic acids extracted from tar sands have been reported to affect female fertility in rats exposed to oral doses of 60 mg/kg/day during pre-breeding, breeding, and gestation (93% success in controls vs. 7% treated). In addition, total cholesterol of the treated group was 30% lower than controls. No fetal malformations were reported (Rogers et al, 2002b –abstract only). The quality of this study cannot be verified since the report does not provide a complete set of experimental details.

Summary: The Testing Group does not think that the data are of sufficient quality to estimate the reproductive or developmental toxicity of naphthenic acids. Naphthenic acids will be tested using a 28-day combined, repeated dose and reproductive/developmental toxicity screening protocol (OECD Test Guideline 422) (See “Repeated Dose Toxicity”).

EVALUATION OF EXISTING PHYSICOCHEMICAL AND ENVIRONMENTAL FATE DATA

Streams Containing Naphthenic Acids

Physicochemical Data

Although some data for products in this subcategory exist, not all of the physicochemical SIDS endpoints are defined and a consensus database for chemicals that represent products in this subcategory does not exist. Therefore, calculated and measured representative data have been identified and a technical discussion provided, where appropriate. The EPIWIN[®] computer model (U.S. EPA, 2000), as discussed in the US EPA document entitled "*The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program*" (U.S. EPA, 1999a) has been used to calculate physical-chemical properties of representative constituents of naphthenic acids.

Because of the diversity of compounds encompassing naphthenic acids, it is not feasible to model the physicochemical endpoints for each potential compound. Modeling efforts were directed towards those constituents of naphthenic acids covering representative molecular weights and isomeric structures most likely to exist in the streams defined in this category.

Melting Point

Because naphthenic acids are not pure chemicals, the melting point characteristics of these complex mixtures vary with the hydrocarbon composition of their make-up. A technical discussion of factors affecting the melting point characteristics provided in the robust summary used information from published sources and modeled values using EPIWIN, MPBPWIN Version 1.40 (U.S.EPA, 2000). Based on data available in commercial product specifications and Material Safety Data Sheets (MSDS), substances produced for commercial use have melting points that fall in the range from –35 °C to +2 °C. Estimated melting points for constituent cycloalkyl carboxylic acids representative of molecular weight and carbon numbered naphthenic acids extracted from petroleum streams ranged from 117 to 160 °C. Actual melting ranges will vary depending upon the constituent hydrocarbons in the naphthenic acid mixture. Additional steps used in the

refining of the commercial products may explain differences among melting points of those products and waste streams.

Summary: No additional testing is proposed. Adequate data are presented to characterize the melting points of naphthenic acid mixtures.

Boiling Point

Because these substances are not pure chemicals, the boiling point characteristics of naphthenic acids and their salts vary according to the hydrocarbon component make-up of the complex mixture. Therefore, a technical discussion of factors affecting the distillation range characteristics was provided in the robust summary using information from published sources and EPIWIN, MPBPWIN Version 1.40 (U.S.EPA, 2000). Based on data available in commercial product specifications and Material Safety Data Sheets (MSDS), substances produced for commercial use have boiling points that fall in the range from 140 °C to 370 °C. Estimated boiling points for constituent cycloalkyl carboxylic acids representative of molecular weight and carbon numbered naphthenic acids extracted from petroleum waste streams ranged from 233 to 375 °C. Actual boiling ranges will vary depending upon the constituent hydrocarbons in the naphthenic acid mixture. Additional steps used in the refining of the commercial products may explain differences in the boiling ranges of those products and waste streams.

Summary: No additional testing is proposed. Adequate data are presented for distillation ranges for naphthenic acids.

Vapor Pressure

Commercial product data typically provided narrative comments such as “negligible”, “very low”, or “not applicable” for vapor pressures of those substances (SocTech 2003; AGS Chemicals Limited 2003; Mallinckrodt Baker Inc. 1997). Because naphthenic acids are complex mixtures, the vapor pressure of the mixture is a function of the sum of the vapor pressures of the components in their pure state times their mole fraction in the mixture (Raoult’s Law). Estimates of the vapor pressures of constituent naphthenic acid compounds reported by Rogers et al. (2002c) to predominate in extracts of oil sands tailings water were made using EPIWIN (U.S. EPA 2000). A technical discussion of those estimates and predicted vapor pressures for naphthenic acid mixtures was developed in the robust summary. Based upon modeled estimates of representative constituent naphthenic acid structures, vapor pressures ranged from 1.8×10^{-3} to 1.4×10^{-5} Pa.

Summary: No additional testing or modeling is proposed. Adequate characterization of vapor pressure for naphthenic acids was developed.

Partition Coefficient

Due to their complex composition, unequivocal determination of the log K_{ow} of naphthenic acid mixtures cannot be made. To gain an understanding of the partitioning potential of these substances, partition coefficients of selected molecular weights and naphthenic ring structures were modeled using EPIWIN[®] (U.S. EPA, 2000). Structures

were selected that have been reported to represent the predominant range of molecular weights and ring constituents of naphthenic acids found in crude oil extracts (Rogers et al. 2002c). Estimates demonstrated that molecules containing longer carboxyl side chains tend to have higher partition coefficients. Also, multi-ring compounds tend to have lower partition coefficients than single-ring compounds of equal molecular weight. Partition coefficients for the modeled naphthenic acid structures ranged from 5 to >6. This range of values is based on structures known to predominate in some naphthenic acid extracts; however, lower partition coefficients would be predicted for structures having lower molecular weights.

Summary: No additional testing or modeling is proposed. Partition coefficients of selected molecular weight naphthenic acids commonly found in complex mixtures were estimated.

Water Solubility

Because naphthenic acids exist as mixtures of many different compounds having a variety of molecular weights, number of cycloalkane rings, and alkyl side chains, the water solubility of substances in this subcategory will depend upon the compositional make-up of the complex mixture (Havre, 2002). Also affecting solubility is the pH of the naphthenic acid solutions. Naphthenic acids are weak acids having pKa values of approximately 5 (CEATAG, 1998; Havre, 2002). The greatest proportion of the total acid in solutions having pHs >5 would exist in the ionic form, while solutions having pHs <5 would exist mostly in the molecular form (Havre, 2002). Therefore, alkaline solutions increase a naphthenic acid's solubility, and acid solutions decrease solubility (Havre 2002).

Data cited in commercial product literature vary widely and suggest that degree of refining in order to meet product performance specifications may greatly influence the solubility of the end product. These product literature reports are largely unassignable with respect to reliability, but they have cited solubility values as high as 5000 mg/l at pH 9 (CEATAG, 1998). In contrast, other product literature references have cited narrative statements such as "very low water solubility" (SocTech S.A., 2003), or "only slightly soluble in water" (AGS Chemicals Limited, 2003).

Because naphthenic acid mixtures may contain hundreds to thousands of individual compounds, the EPIWIN[®] computer model was used to estimate a range of water solubility values for selected naphthenic acid structures reported by Rogers et al. (2002c) to predominate in some natural naphthenic acid extracts. A technical discussion was prepared in the robust summary to describe factors affecting the water solubility of these substances. Estimated solubility values ranged from 0.0003 to 2.1 mg/l depending upon the molecular weight.

Summary: No additional testing or modeling is proposed. Water solubility values of selected molecular weight naphthenic acids commonly found in complex mixtures were presented.

Photodegradation

Atmospheric oxidation as a result of hydroxyl radical attack is indirect photodegradation. Substances in this subcategory have low vapor pressures and therefore do not have a tendency to volatilize to air where they can undergo reactions with photosensitized oxygen in the form of hydroxyl radicals (OH^\cdot). Therefore, these reactions are not expected to be an important environmental fate process.

The potential to undergo indirect photodegradation was estimated using the atmospheric oxidation potential (AOP) model subroutine (AOPWIN V1.90) in EPIWIN[®] (U.S.EPA, 2000), which calculates a chemical half-life and an overall OH^\cdot reaction rate constant based on a 12-hour day and a given OH^\cdot concentration. Atmospheric oxidation rates and half-lives were thus calculated for a range of molecular weight and naphthenic ring structures covering one to four-ring cycloalkyl carboxylic acids having molecular weights from 254 to 325. These structures were considered appropriate because they have been found to predominate in naphthenic acid extracts from Athabasca oil sands, a source considered high in naphthenic acid content (Rogers et al., 2002c).

AOP half-life estimates for these compounds ranged from 0.3 to 0.6 days and show a lack of persistence in the atmosphere. However, with vapor pressures of 1.8×10^{-3} to 1.4×10^{-5} Pa, there is low potential for these substances to partition to the atmosphere where indirect photodegradation would occur.

Summary: No additional modeling is proposed. The atmospheric oxidation potential of representative components in naphthenic acids has been estimated.

Stability in Water

Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters (Harris, 1982). Because naphthenic acids do not contain significant levels of these functional groups, components in the naphthenic acid subcategory are not subject to hydrolysis.

Summary: No additional modeling is proposed. Components in the naphthenic acids subcategory do not undergo hydrolysis.

Chemical Transport and Distribution (Fugacity Modeling)

Fugacity-based multimedia modeling can provide basic information on the relative distribution of chemicals between selected environmental compartments (e.g., air, water, soil, sediment, suspended sediment and biota). The U.S.EPA has agreed that computer modeling techniques are an appropriate approach to estimating chemical partitioning (fugacity is a calculated endpoint and is not measured). A widely used fugacity model is the EQC (Equilibrium Criterion) model (Mackay 1991). The EQC model is a Level 1 (i.e., steady state, equilibrium, closed system and no degradation) model that utilizes the input of basic chemical properties including molecular weight, vapor pressure, and water solubility to calculate distribution within a standardized regional environment. EPA cites

the use of this model in its document “Determining the Adequacy of Existing Data” that was prepared as guidance for the HPV chemicals program (U.S. EPA, 1999b).

To gain an understanding of the potential transport and distribution of naphthenic acids, the EQC model was used to characterize the environmental distribution of different molecular weights and structural conformations of naphthenic acid molecules. These constituents were selected because they had been shown to predominate in extracts of Athabasca oil sands (Rogers et al., 2002c). Modeling results show that when naphthenic acids are released to the environment, they would bind to soil/sediments, with negligible fractions partitioning to air, water or biota. However, not all naphthenic acids are composed of identical chemical species as reported by Rogers et al. (2002c), and mixtures having a predominance of low molecular weight constituents would be expected to partition to some degree to water depending on their pKa characteristics and the pH of the water.

Summary: No further modeling is proposed. Fugacity modeling has been done to provide an estimate of the percent distribution in environmental media of various molecular weight and ring-structured naphthenic acids.

Biodegradation

Although no standardized ready or inherent biodegradation studies were available for naphthenic acids, research has shown these materials to be amenable to microbial utilization similar to other hydrocarbon compounds. Studies have demonstrated that microorganisms indigenous to oil sands tailings were capable of degrading complex mixtures of commercial sodium salts of naphthenic acids as well as mixtures of organic acids extracted from oil sands tailings (Herman et al., 1993, 1994). Although rates of biodegradation may be affected by steric factors related to the numbers of cycloalkane rings or the alkyl constituents on the ring structure, microbial populations respond to naphthenic acid substrates through increased CO₂ production, O₂ consumption, and enhancement of metabolism with the addition of nutrients. With single-ring naphthenic acids, biodegradation of both the ring and side-chain acid has been shown to occur (Herman et al., 1993, 1994). As the number of cycloalkane rings increase, it may be inferred from what is known about degradation of multi-ring naphthenes that biodegradation rates may slow, but these substances will degrade given time (Bartha and Atlas 1977). Biodegradation (as percent of organic carbon converted to CO₂) of model naphthenic acid compounds, cyclohexane carboxylic acid, cyclohexane pentanoic acid, 2-methyl cyclohexane carboxylic acid, and *trans*-4-pentylcyclohexane carboxylic acid ranged from 6 to 67% depending on the micro-organism culture and the presence of nitrogen and phosphorus nutrients in the medium (Herman et al., 1994).

Summary: No further testing is proposed. An adequate characterization of the potential for naphthenic acid biodegradation to occur has been made. A technical review of current research on microbial utilization of naphthenic acids has been included in the robust summary.

EVALUATION OF EXISTING ECOTOXICITY DATA AND PROPOSED TESTING

Streams Containing Naphthenic Acid

Aquatic toxicity endpoints for the OECD SIDS/HPV Chemical Program include acute toxicity to a freshwater fish and invertebrate, and toxicity to a freshwater alga. There are no standard guideline studies on the toxicity of naphthenic acids to these aquatic organisms. Toxicity endpoints reported in the literature largely report nominal lethal concentrations with varying amounts of supporting information on test conditions. The available data show that naphthenic acids are moderately to highly toxic to fish. Cairns et al. (1965) reported the 96-hour TLM of 16.3 mg/l for adult zebra fish (*Brachydanio rerio*) and the 48-hour TLM of 3.5 mg/l for embryos based on nominal concentrations. Dorn (1992) found the 96-hour LC50 for three-spine sticklebacks (*Gasterosteus aculeatus*) to be between 2.5 and 5 mg/l also based on nominal concentrations. Other data not considered to provide sufficient detail for assessment included a report of a 48-hour TLM for bluegill (*Lepomis macrochirus*) of 5.6 mg/l (Cairns and Scheier, 1962) and a report of a 96-hour LC50 for bluegill of 0.0026 mg/l (Exxon 1980a).

No studies were found that measured acute toxicity to freshwater invertebrates or algae.

Summary: The Testing Group intends to conduct the following studies on naphthenic acids: OECD Guideline 203, Fish Acute Toxicity Test; Guideline 202, Daphnia sp., Acute Immobilization Test; and Guideline 201, Alga Growth Inhibition Test.

MATRIX OF AVAILABLE ADEQUATE DATA AND PROPOSED TESTING

TABLE 1: Naphthenic Acid: Matrix of Available Data and Proposed Testing

TEST	DATA ASSESSMENT
Physical/Chemical Properties	
Melting Point	Adequate
Boiling Point	Adequate
Vapor Pressure	Adequate
Partition Coefficient	Adequate
Water Solubility	Adequate
Environmental Fate	
Photodegradation	Adequate
Stability in Water	Adequate
Chemical Transport and Distribution (Fugacity Modeling)	Adequate
Biodegradation	Adequate
Ecotoxicity	
Algae Growth Inhibition	TEST
Acute Feshwater Invertebrate	TEST
Acute Freswater Fish	TEST
Mammalian Toxicity	
Acute	Adequate
Repeat Dose	TEST
Genetic Toxicity, <i>In vitro</i>	Adequate
Genetic Toxicity, <i>In vivo</i>	TEST
Repro/Development	TEST

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